Hyperalkaline speleothem from Derbyshire: new observations on morphology and growth crystallisation

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Unusual speleothem formation, associated with hyperalkaline (pH>12) groundwaters have formed within a shallow abandoned railway tunnel at Peak Dale, Derbyshire. The hyperalkaline groundwaters are produced by the leaching of a thin layer (1-2 m) of old lime kiln wastes that were dumped on the soil-bedrock surface above the tunnel. Rainwater percolating through this lime waste leaches portlandite ($Ca(OH)_2$) formed by the hydration of lime (CaO) and potentially other clinker phases in the limewaste (e.g. calcium silicates and aluminates), giving rise to high pH Ca-OH-type groundwater that is close to portlandite-saturation (approximately pH 12.5), which discharges through fractures in the roof of the tunnel below. This setting causes a different reaction and chemical process to that associated with the formation of traditional calcium carbonate speleothems formed from Ca-HCO_3-type groundwaters normally associated with limestone.

At pH 12.5 any carbonate species in solution will be dominated by CO_3^{2-} rather than HCO_3^-. Furthermore, the solubility of $CaCO_3$ in these Ca-OH-type dripwaters is extremely low, and therefore CO_2 is sequestered from the atmosphere resulting in the following reaction:

$$Ca^{2+}_{(aq)} + OH^-_{(aq)} + CO_{2(g)} \leftrightarrow CaCO_{3(s)} + H^+_{(aq)}$$

Stalagmites within this tunnel have an unusual morphology comprising a central sub-horizontally-laminated column of micro- to nano-crystalline calcium carbonate encompassed by an outer sub-vertical ripple-laminated layer. We present the results of a detailed petrological study of the morphology and formation mechanisms of these stalagmites. The stalagmites are composed of calcite, which is shown to be a secondary phase; some pseudomorphs of vaterite are present (<5 μm) but the bulk of the stalagmites comprises larger pseudomorphs (<1 mm) which we believe to be after ikaite (calcium carbonate hexahydrate: $CaCO_3.6H_2O$). Ikaite is often referred to as the 'cold climate calcium carbonate polymorph' (Marland 1975); the first naturally occurring example was identified in Ikka Fjord in Southwest Greenland (Pauly 1963). This polymorph is metastable at ambient pressures and temperatures. However, the tunnel has a constant temperature of 8 ^oC which is above the potential crystallisation temperatures suggested by experimental work which indicates precipitation occurs at temperatures close to zero (Bischoff et al. 1993). Analysis of a stalagmite actively growing at the time of sampling and preserved immediately following sampling within a dry nitrogen cryogenic vessel, suggests that decomposition to calcite is almost instantaneous following crystallisation of ikaite. Although ikaite has recently been discovered forming during cold weather in superficial tufa deposits associated with high pH springs discharging from lime waste (Milodowski et al., 2014), we believe this is the first occurrence of this calcium carbonate polymorph observed within speleothem.

Bischoff, J. L., et al. (1993). The solubility and stabilization of ikaite ($CaCO_3.6H_2O$) from 0° to 25°C: environmental and paleoclimatic implications for thinolite tufa. The Journal of Geology 101(1): 21-33.

Marland, G. (1975). The stability of $CaCO_3.6H_2O$ (ikaite)" Geochimica et Cosmochimica Acta 39(1): 83-91.

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Pauly, H. (1963) "Ikaite", a new mineral from Greenland. Arctic, 16: 263-264